



TITLE:

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CITATION:

Terao, Jun ...[et al]. Synthesis of functionalized insulated molecular wires by polymerization of an insulated π -conjugated monomer.. Chemical communications 2013, 50(6): 658-660

ISSUE DATE:

2013-11-07

URL:

<http://hdl.handle.net/2433/196810>

RIGHT:

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Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Synthesis of functionalized insulated molecular wires by polymerization of an insulated π -conjugated monomer**

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⁵ Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

DOI: 10.1039/b000000x

A new method for the synthesis of an insulated π -conjugated monomer was developed via the sequential self-inclusion followed by the elongation of the π -conjugated unit. The monomer was utilized in the synthesis of stimuli-responsive insulated molecular wires.

The field of molecular electronics is the most promising area for further innovation in information technology.^{1,2} In molecular electronics, each functionalized molecule has the potential to behave as a single device, such as a switch,³ socket,⁴ memory,⁵ light emitter,⁶ sensor,⁷ or transistor,⁸ which enables extensive integration and miniaturization. To realize such molecular electronics, various functionalized molecules must be wired between electrodes with nanosized gaps, in an efficient and dense fashion.^{3,9–12} Therefore, the development of techniques for the synthesis of definite-structure molecular wiring materials with appropriate functional groups and the development of an effective molecular wiring method is eagerly anticipated. In this context, our current research focuses on the synthesis of insulated molecular wires (IMWs)^{13–18} possessing high linearity, rigidity, stability, and high charge mobility.^{19–22} Herein, we report a new synthetic method for producing functionalized IMWs by polymerization of highly insulated oligo(phenylene ethynylene) (OPE) as a monomer.

The initial step of the current protocol was the design and synthesis of an insulated π -conjugated monomer based on the following considerations: (1) Permethyl α -cyclodextrin (PM α -CD), used as a covering material, introduces high organic solubility; (2) π -conjugated OPE units provide the desired highly linear and rigid structure; and (3) the [3]rotaxane structure fixed by tether units is characterized by a high covering ratio and perfect structural regularity. We previously synthesized IMWs bearing poly(phenylene ethynylene) (PPE) units by the copolymerization of pseudo-linked [3]rotaxane **1** (Figure 1) with 1,4-diiodobenzene.²⁰ In this method, a hydrophilic solvent system was required because the inclusion complex **1** was formed by hydrophilic-hydrophobic interactions. When we tried to prepare functionalized IMWs by the copolymerization of **1** with other functionalized π -conjugated diiodides instead of 1,4-diiodobenzene, we failed to obtain the desired products because of the steric hindrance issue and the insolubility of the diiodides in the hydrophilic medium. To overcome these problems, we tried to synthesize the insulated OPE **3** as a monomer having a fixed [3]rotaxane structure in the organic solvents. The synthetic route

for generating the desired **3** is shown in Figure 1. Sequential self-inclusion of **1'** in a hydrophilic solution ($\text{H}_2\text{O}/\text{MeOH} = 1/2$) provided the pseudo-linked [3]rotaxane **1**.²⁰ A Sonogashira coupling reaction was used to fix the pseudo-linked [3]rotaxane structure by elongating the OPE unit: **1** was treated with *tert*-butyldimethylsilyl (TBS)-protected *p*-iodophenylacetylene in the presence of catalytic amounts of $\text{Pd}(\text{OAc})_2$, tris(4,6-dimethyl-3-sulfonatophenyl)phosphine trisodium salt (TXPTS), and CuI . After deprotection of the TBS groups in **2** with tetra-*n*-butylammonium fluoride (TBAF), the desired insulated monomer **3** was obtained in high yield. The fixed [3]rotaxane structure was confirmed through analysis by ^1H NMR analysis and ROESY NMR (see Supporting information, Figures SI1 and SI2). Highly insulated OPE monomer **3** was soluble in various organic solvents and stable under reflux in toluene for 24 h without decomplexation, despite the lack of bulky stopper groups at the ends of the π -conjugated guest unit.

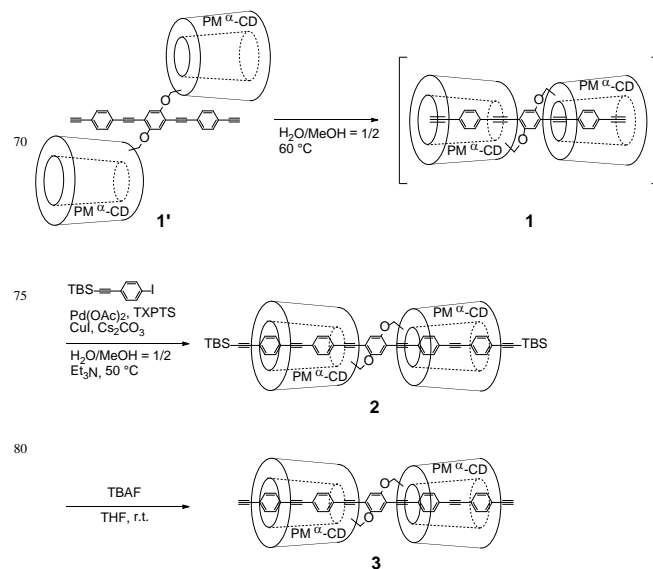


Figure 1. Synthesis of insulated π -conjugated monomer.

The synthesis of insulated poly(phenylene ethynylene) (PPE) was executed via Sonogashira copolymerization of **3** with 1,4-diiodobenzene in the presence of a catalytic amount of $\text{Pd}_2(\text{dba})_3$ and PPh_3 in the organic medium ($\text{THF}/\text{Et}_3\text{N} = 2/1$). The weight-average molecular weight (M_w) and polydispersity index

(PDI) of the insulated PPE **4** were 1.21×10^5 and 3.21, respectively, determined by an absolute molecular weight determination technique using size-exclusion chromatography (SEC) with a low angle (7°) light-scattering detector. The average degree of polymerization (\bar{n}) was found to be 40. Bithiophene, tetrafluorobenzene, or benzothiadiazole units could be introduced into the polymer backbone of the IMW using the corresponding dihalides as monomers, giving rise to **5**, **6**, and **7**, respectively (Figure 2). The wavelengths of the absorption and emission maxima increased in the order $7 < 4 < 6 < 5$, reflecting the extent of conjugation in the polymer backbones of these species (Figures SI3a and SI3b). This method was subsequently applied to the synthesis of stimuli-responsive IMWs by Sonogashira copolymerization of **3** with functionalized dihalides having a tetrathiafulvalene (TTF) unit as a redox group, a porphyrin unit as a metal-ion sensing group, and an azobenzene or diarylethene unit as a photoswitching group. These reactions gave rise to **8**, **9a-c**, **10**, and **11**, respectively (Figure 2).

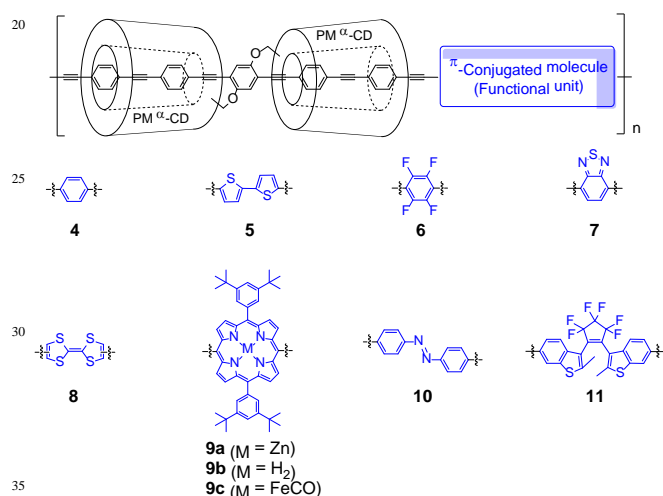


Figure 2. Structures of functionalized insulated molecular wires.

The responses of these polymers to external stimuli were examined by first monitoring the change in the emission spectrum of functionalized IMW **8** bearing TTF moieties in response to redox manipulation, as shown in Figure 3. A seven-fold increase in the emission intensity of polymer **8** was observed in response to oxidation of the TTF moieties via the addition of the oxidizing reagent $\text{Fe}(\text{ClO}_4)_3$. Subsequent reduction of the oxidized TTF moieties with reducing agent FeCp_2 returned the intensity to the initial level. This emission switching phenomenon can be attributed to photo-induced electron transfer (PET).²³ Before oxidation and after reduction, an electron in each polymer should be transferred from the HOMO of the TTF moiety to the HOMO of the excited insulated OPE moiety via the PET mechanism, with consequent inhibition of the fluorescence emission. However, after oxidation, the fluorescence emission should be observed from the polymer because oxidation of the TTF moieties to the di-positive state lowers the HOMO levels and, therefore, inhibits PET (Figure SI4a). Interestingly, however, no significant change in the emission intensity of the corresponding un-insulated polymer **8'** was observed for the same redox reaction. The lack of emission switching in **8'** was probably due to the higher HOMO level of the

un-insulated OPE moiety relative to that of the insulated species, and thus, PET was ineffective regardless of the oxidation state of the TTF moieties (Figure SI4b). Insulation constrains the conformation of the OPE chain in a somewhat twisted orientation, which prevents the delocalization of electrons along the conjugated chain and results in a decrease in the HOMO level (Figure SI5).²⁴

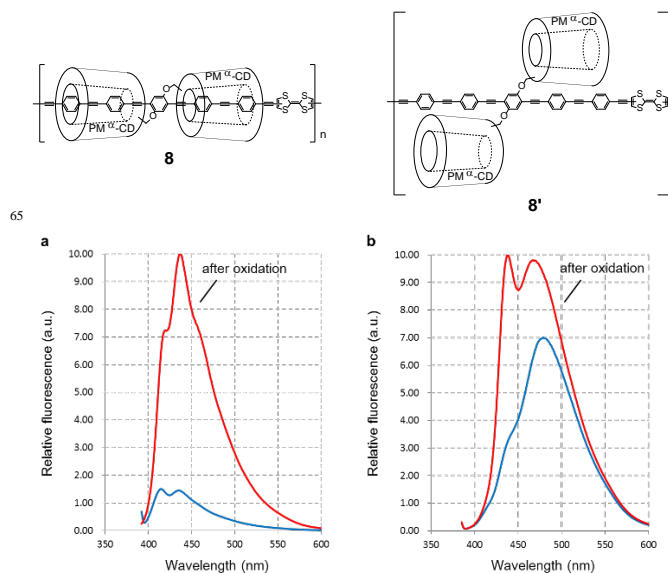


Figure 3. a,b) Fluorescence spectra of polymer **8** and **8'** in CHCl_3 in different redox states: natural form (blue) and di-cation form (red).

Treatment of the zinc porphyrin IMW **9a** with acid generated the corresponding non-metallated porphyrin IMW **9b**. The difference in the charge mobilities of the metallated and non-metallated porphyrin IMWs was examined in the solid state by time-resolved microwave conductivity (TRMC) measurements (Figure 4a).²⁵ In contrast to the conductivity transient observed for non-metallated porphyrin IMW **9b**, zinc porphyrin IMW **9a** exhibited a longer lifetime for the charged species on its backbone, with a clear signature of delayed charge carrier formation. This may have been due to the lowering of the SOMO with high symmetry (Figures SI7a and SI7b) by introduction of the metal center, as predicted by density functional theory (DFT) calculations. After zinc was re-introduced into the porphyrin center by treating **9b** with $\text{Zn}(\text{OAc})_2$, the conductivity transient measured using TRMC led to a result that was identical to the result observed for **9a**. On the other hand, iron porphyrin IMW **9c**, formed by the treatment of **9b** with FeCl_2 and carbon monoxide, exhibited the highest photoconductivity transients, with extremely long lifetimes for the charged species (Figures 4a and SI7c). Because of the remarkable potential of IMW **9c** as a one-dimensional semiconductor material, its intramolecular charge carrier mobility was quantitatively assessed by combining TRMC and transient absorption spectroscopy (TAS) measurements (Figures 4b, 4c, and SI7d). The partial overlap of the triplet absorption (570 and 750 nm) was considerable at 570 nm,²⁶ and therefore, the charge carrier generation yield ϕ was overestimated to be 5×10^{-3} at 20 μs after pulse exposure, where the contribution from the triplet excited states to the conductivity transient was negligible. The shorter lifetime of the triplet excited states in the present case was due to triplet-triplet annihilation leading to free charge carriers on the backbone of **9c**. In this case,

the rise time of the transient conductivity (Figure 4a) was identical to that of the optical transients of the triplet excited states. The intramolecular hole mobility values were estimated to be as high as $0.1 \text{ cm}^2/(\text{V s})$ ($0.3 \text{ cm}^2/(\text{V s})$ along the **9c** backbone), which indicated the existence of effective conductive pathways for positive charges along the backbones of the iron–metallated porphyrin moieties. These results also indicated that the porphyrin IMWs switch both the stability and mobility of positive charges on their backbones in response to variations of the coordinated metal ion and to the absence or presence of a metal ion. Thus, it is expected that this IMW could be applied to ion–sensing devices. As shown in Figure 4d, a considerable enhancement in the transient conductivity signal was observed for the zinc porphyrin IMW **9a** film annealed under oxygen atmosphere, reaching a value four times that of the end-of-pulse conductivity. The saturated concentration of oxygen in the present case can be predicted to be five-fold higher than that of the ambient (air-saturated) atmosphere; this is in striking agreement with the initial yield of the charge carriers evolved via rapid photo-induced electron transfer reactions (within the time constraint of the present setup). Molecular oxygen is well known as an effective quencher of the triplet excited state, and the considerable increase in the TRMC signal also supported the negligibly small contribution from the triplet excited states of **9a**.

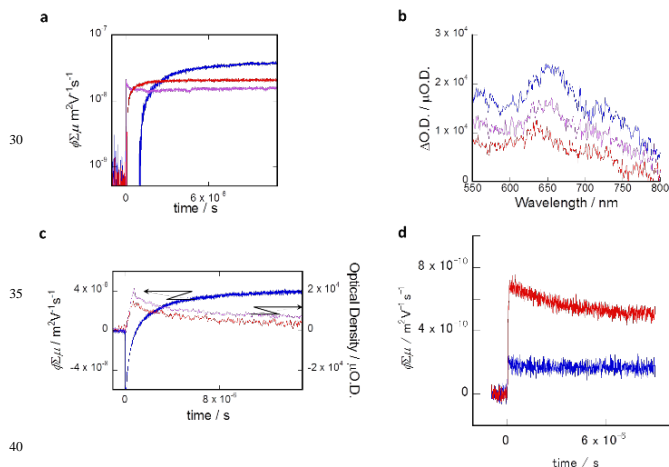


Figure 4. a) Conductivity transients observed upon excitation of cast films of **9a** (red), **9b** (violet), and **9c** (blue) at 355 nm using 1.9×10^{15} photons cm^{-2} , film thicknesses of 0.9–2.3 μm , and ambient conditions. b) Transient absorption spectra of **9c** at 1 (blue), 3 (violet), and 10 (red) μs after pulse excitation at 355 nm (2.4×10^{16} photons cm^{-2}). c) Kinetics traces for the transient conductivity (blue) and optical absorption at 670 nm (violet) and 570 nm (red) in the **9c** solid film. d) Conductivity transients observed upon excitation at 355 nm at 1.8×10^{16} photons cm^{-2} in a cast film of **9a** under ambient conditions (blue) and O_2 (red). The casted plate was placed in a TRMC probe under O_2 at 70°C for 1 h and then cooled to room temperature before transient conductivity measurement under O_2 .

Conclusions

In summary, we designed and synthesized novel organic–soluble insulated OPE monomers. Stimuli-responsive IMWs^{27,28} with three different functions—redox switching, ion sensing, and photoswitching—were successfully constructed using the novel insulated OPE monomers.

Notes and references

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- † Electronic Supplementary Information (ESI) available: See DOI: 10.1039/b000000x/
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